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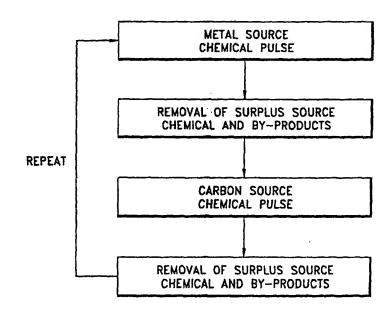
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(54) Title: DEPOSITION OF TRANSITION METAL CARBIDES



(57) Abstract: The present invention relates generally to a method of depositing transition metal carbide thin films. In particular, the invention concerns a method of depositing transition metal carbide thin films by atomic layer deposition (ALD), in which a transition metal source compound and a carbon source compound are alternately provided to the substrate. A variety of metal and carbon source gases are disclosed. The methods are applicable to forming metal carbide thin films in semiconductor fabrication, and particularly to forming thin, conductive diffusion barriers (6) within integrated circuits having trench (1) and via (2) openings.



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DEPOSITION OF TRANSITION METAL CARBIDES

Background of the Invention

Field of the Invention

The present invention relates to the deposition of transition metal carbide thin films. More specifically, the present invention relates to the use of sequential self-saturating surface reactions to form transition metal carbides on various substrates.

Description of the Related Art

Carbides of transition metal elements in groups 4 (Ti, Zr, Hf), 5 (V, Nb, Ta) and 6 (Cr, Mo, W) of the periodic table possess several attractive properties. They are relatively inert, have very high melting points, are extremely hard and wear resistant, and have high thermal conductivity and metal-like electrical conductivity. For these reasons, transition metal carbides have been proposed for use as low resistance diffusion barriers in semiconductor fabrication (see, e.g., international patent application WD 00/01006; U.S. Patent No. 5,916,365).

General information about metal carbides can be found, for example, in Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, Vol. A5, VCH Verlagsgesellschaft, 1986, pp. 61 - 77, and in the Kirk-Othmer Encyclopedia of Chemical Technology, 4th Edition, Vol. 4, John Wiley & Sons, Inc., 1992, pp. 841 - 878. Transition metal carbides can have a wide range of compositions. Ordered and disordered carbon deficient forms exist, of which the tungsten carbides W₃C, W₂C, WC and WC_{1-x} are examples. In these forms, carbon resides in the interstitial cavities between metal atoms.

Suggested deposition methods include Chemical Vapor Deposition (CVD), Metal Organic Chemical Vapor Deposition (MOCVD) and Physical Vapor Deposition (PVD).

Carbides have been deposited by CVD type processes wherein more than one source chemical is present in the reaction space at the same time. A CVD method of depositing tungsten carbide from tungsten hexafluoride, hydrogen and a carbon-containing gas has been described, for example, in international patent application WO 00/47796. The carbon-containing gas is initially thermally activated. All of the gaseous source chemicals are present at the same time in the reaction space, resulting in the deposition of nonvolatile tungsten carbide on the substrate. A CVD reaction of WF₆ with trimethylamine and H₂ has been disclosed for yielding WC films at 700°C · 800°C and beta-WC_{1,x} films at 400°C · 600°C (Nakajima et al., <u>J. Electrochem. Soc.</u> 144:2096·2100 (1997)). The H₂ flow rate affects the deposition rate of tungsten carbide. One problem with the disclosed process is that the substrate temperature is rather high relative to thermal budgets for state-of-the-art semiconductor fabrication, particularly in metallization stages.

MOCVD processes utilize organometallic compounds that are thermally decomposed on the substrate or combined with other organic compounds in gas phase and then contacted with the substrate thus breaking the source chemical molecules and forming the final product. Tungsten carbide has also been deposited on substrates by the thermal decomposition of organotungsten derivatives of W(CO)₆ at low pressures (Lai et al., Chem. Mater. 7:2284-2292 (1995)). Similarly, TiC has been deposited in a CVD process by the thermal decomposition of organometallic

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titanium compounds (Girolami et al., <u>Mater. Res. Soc. Symp. Proc.</u> 121:429-438 (1988)). U.S. Patent No. 5,916,365 also discloses thermal decomposition of pentadimethyl-aminotantalum. In these processes, the source chemical molecules contain both the metal and the carbon. However it's utility on complex, irregular surfaces is not known.

PVD processes generally deposit along a line-of-sight. One method of depositing tantalum carbide for a diffusion barrier layer by PVD has been described in U.S. Patent No. 5,973,400. The tantalum carbide layer was formed by sputtering tantalum or tantalum carbide under N₂/CH₄/Ar atmosphere. Line of sight deposition, however, means that complex substrate contours will have insufficient thin film coverage in shaded areas. Additionally, line-of-sight deposition means that low-volatility source material arriving directly from the source to the substrate will likely adhere to the first solid surface that it encounters, thus producing low-conformality coverage.

Thus, there is a need in the art for improvements in methods of depositing transition metal nitrides.

Summary of the Invention

In accordance with one aspect of the invention, a method is disclosed for depositing a transition metal carbide thin film by an atomic layer deposition (ALD) process. In the illustrated embodiment, vapor-phase pulses of at least one transition metal source compound and at least one carbon source compound are alternately fed into a reaction space containing a substrate.

The transition metal source compound preferably comprises a metal source gas selected from the group consisting of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W. An exemplary transition metal source gas is a metal halide, such as tungsten hexafluoride. Exemplary carbon source compounds include boron compounds, silicon compounds and phosphorous compounds. Desirably, in these exemplary source gas compounds, either boron, silicon or phosphorus bond directly to carbon.

The process is of particularly utility when depositing ultrathin, high quality layers, such as typically demanded in the field of semiconductor fabrication. For example, a metal carbide thin film can advantageously form thin diffusion barrier that is conductive and conformal over integrated circuit topography (e.g., dual damascene trenches and vias).

Brief Description of the Drawings

Figure 1 presents a schematic view of a dual damascene structure and the placement of the metal carbide diffusion barrier.

Figure 2 presents a flow chart of the metal carbide ALD process.

Detailed Description of the Preferred Embodiment

For the purpose of the present invention, an "atomic layer deposition" or "ALD" type process designates a process where the deposition of thin film onto a substrate is based on sequential and alternating self-saturating surface reactions. The principles of ALD are disclosed, e.g., in U.S. Patent Nos. 4,058,430 and 5,711,811, the disclosures of which are hereby incorporated by reference herein.

"Substrate temperature" means a temperature that is maintained in the reaction space during the deposition process.

"Transition metals" means elements of groups 3 to 12 of the periodic table of the elements. A preferred subset of the transition metals are those of groups 5 (titanium, zirconium and hafnium), 6 (vanadium, niobium and tantalum) and 7 (chromium, molybdenum and tungsten) of the periodic table of the elements. Metal carbides of these elements contain interstitial carbon and have some of the properties of pure metals.

"Reaction space" is used to designate a reactor or reaction chamber in which the conditions can be adjusted so that deposition by ALD is possible.

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In the preferred embodiment of the present invention, transition metal carbide thin films are prepared by a chemical gaseous deposition process. The preferred chemical gaseous deposition process is an atomic layer deposition (ALD) type process. The principles of ALD are well known to those skilled in the art.

According to a preferred ALD type process, a transition metal carbide thin film is grown on a substrate placed in a reaction space at an elevated temperature. Thus, a substrate is preferably placed in a reaction space and is subjected to sequential, alternately repeated surface reactions of at least two vapor-phase reactants such that a transition metal carbide thin film grows on the substrate. Preferably, the conditions in the reaction space are adjusted so that no gas-phase reactions, i.e., reactions between gaseous reactants, occur. In the preferred ALD type process, a metal source compound and a carbon source compound are alternately fed to the reaction space in gaseous form such that they are not present simultaneously in the gas phase in the reaction space. Thus, only surface reactions between species or complexes adsorbed by chemisorption on the surface of the substrate and gaseous reactants are allowed. The reactions are preferably self-saturating and self-limiting.

In the preferred ALD type process, the vapor-phase pulses of the transition metal source compound and the carbon source compound are alternately and sequentially fed into the reaction space and brought in contact with the surface of the substrate. The source compounds are preferably fed into the reaction space with the aid of an inert or noble carrier gas, such as nitrogen or argon. The "surface" of the substrate initially comprises the substrate material. In one embodiment the substrate has been pretreated in advance, e.g., by contacting it with a chemical for modifying the surface properties thereof. Once a transition metal carbide layer has been deposited, it forms the surface for any subsequent transition metal carbide layers.

One pulsing sequence or "cycle" is depicted in Figure 2. Each cycle in the deposition preferably comprises:

feeding a vapor-phase pulse of a transition metal source compound into the reaction space in an inert carrier gas;

removing the surplus transition metal source compound and any gaseous by-products from the reaction space (e.g., by purging with an inert gas);

feeding a vapor-phase pulse of a carbon source compound into the reaction space in an inert carrier gas; and

removing the surplus carbon source compound and any gaseous by-products from the reaction space (e.g., by purging with an inert gas).

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The cycle may be repeated as many times as desired to produce a transition metal carbide film of the desired thickness. The purging time is preferably selected to be long enough to prevent gas phase reactions and to prevent transition metal carbide thin film growth rates higher than one lattice constant of the transition metal carbide per cycle.

In one embodiment the deposition is carried out at atmospheric pressure. However, it is preferable to carry out the deposition at reduced pressure. The pressure in the reactor is preferably about 0.01 mbar to 50 mbar, and more preferably about 0.1 mbar to 10 mbar. The substrate temperature is preferably low enough to prevent thermal decomposition of the gaseous reactants. On the other hand, the substrate temperature is preferably high enough to avoid the physisorption, or condensation of the source materials. Further, the substrate temperature is preferably sufficiently high to provide the activation energy for the surface reaction. The temperature of the substrate is preferably about 200°C to 600°C, and more preferably about 250°C to 400°C. However, one skilled in the art will recognize that the most preferable substrate temperature and reaction space pressure will depend on the identity of the reactants and the substrate.

If the partial pressure of the gaseous source compound exceeds the condensation limit at the substrate temperature, controlled, layer-by-layer growth of the transition metal carbide film is lost. Thus in the preferred embodiment the temperature of the source container is preferably set below the substrate temperature.

In the preferred embodiment, the transition metal source compound is chemisorbed on the substrate surface, forming a surface bound transition metal complex. The amount of reactants bound to the surface of the substrate by chemisorption will be determined by the surface itself. The reactant molecules will bind to the surface until no more available binding sites remain on the surface, and terminating ligands on the monolayer are non-reactive with excess source compound still in the vapor phase. This phenomenon is known as "self-saturation". Depending on the reactant employed, the physical size of the reactant molecules may prevent complete coverage of the surface when all of the binding sites are occupied. However, the preferred coverage on the substrate is obtained when no more than a single layer of transition metal source complex is adsorbed per pulsing sequence. Thus, several cycles may be necessary to produce a complete monolayer of transition metal carbide.

In a commercial production setting, the amount of time available for the self-saturating reactions is limited mostly by economic factors. For example, the required substrate throughput time for economic efficiency will impose a limit on the time available for the self-saturating reactions.

The substrate may be composed of any material known in the art. Examples include silicon, silica, coated silicon, metals, metal nitrides, metal oxides, porous materials, silicon carbide and silicon nitride. As discussed above, in the preferred embodiment, once a transition metal carbide thin film layer has been deposited by the present method, that layer will form the substrate surface for any subsequent layer.

The transition metal source compound and the carbon source compound are preferably chosen so that the requirements for sufficient vapor pressure, thermal stability at the substrate temperature and sufficient reactivity of the compounds on the substrate surface are fulfilled. Sufficient vapor pressure means that there are enough source

compound molecules in the gas phase near the substrate surface to enable self-saturated reactions at the surface. Sufficient thermal stability means that the source chemical itself does not form growth-disturbing condensable phases on the substrate or leave harmful levels of impurities on the substrate surface through thermal decomposition. Thus, the reactants are preferably chosen to avoid uncontrolled condensation of atoms or molecules on the substrate.

According to the preferred embodiment of the present invention, a transition metal source material and a carbon source material are required. The carbon source material is preferably a boron source compound, a silicon source compound or a phosphorus source compound. However in one embodiment plasma is used and the preferred carbon source material is a hydrocarbon.

1. Transition Metal Source Materials

The preferred metal source compounds are transition metal compounds that are volatile at sufficiently low source temperatures. These transition metal compounds preferably comprise a transition metal selected from the group consisting of W, Ti, Zr, Hf, V, Nb, Ta, Cr and Mo. More preferably, the metal source compounds are metal halides, including metal fluorides and metal chlorides. In an illustrated preferred embodiment, the metal source material is tungsten hexafluoride.

15 2. Boron Source Compounds

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The preferred boron source compounds are boron compounds that comprise at least one carbon atom and that are volatile at temperatures below the substrate temperature. More preferably the boron source materials are boron compounds that have at least one boron-carbon bond in the boron source compound molecule.

The boron source compound is preferably chosen from the following:

Carboranes according to formula I.

 $C_2B_nH_{n-1}$ (I)

Wherein n is an integer from 1 to 10, preferably from 2 to 6, and

x is an even integer, preferably 2, 4 or 6.

Examples of carboranes according to formula 1 include *closo*-carboranes ($C_2B_nH_{n-2}$), *nido*-carboranes ($C_2B_nH_{n-2}$), *nido*-carboranes ($C_2B_nH_{n-2}$).

Amine-borane adducts according to formula II.

R₃NBX₃ (II)

Wherein R is linear or branched C1 to C1D, preferably C1 to C4 alkyl or H, and

X is linear or branched C1 to C10, preferably C1 to C4 alkyl, H or halogen.

Aminoboranes where one or more of the substituents on B is an amino group according to formula III.

R₂N ((())

Wherein R is linear or branched C1 to C10, preferably C1 to C4 alkyl or substituted or unsubstituted aryl group.

An example of a suitable aminoborane is (CH₃)₂NB(CH₃)₂.

Alkyl borons or alkyl boranes, wherein the alkyl is typically linear or branced C1 to C10 alkyl, preferably C2 to C4 alkyl.

The alkylboron compounds are especially preferred. In the preferred embodiment the boron source material is triethylboron (CH_3CH_2)₃B.

3. Silicon Source Compounds

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The preferred silicon source materials are carbon-containing silicon compounds that are volatile at temperatures below the substrate temperature. More preferably silicon source materials are silicon compounds that have at least one silicon-carbon bond in the silicon source chemical molecule. Even more preferably the silicon source materials are alkylsilicon compounds.

4. Phosphorus Source Compounds

The preferred phosphorous source materials are carbon-containing phosphorus compounds that are volatile at temperatures below the substrate temperature. More preferably the phosphorus source materials are phosphorus compounds that have at least one phosphorus-carbon bond in the phosphorus source chemical molecule. Even more preferably the phosphorus source materials are alkylphosphorus compounds.

5. Hydrocarbons

Hydrocarbons with a high hydrogen/carbon ratio are preferably used as carbon source chemicals. More preferably, linear or branched alkanes are used as carbon source chemicals.

In a preferred embodiment, the metal source gas and the carbon source gas do not exist in the gas phase in the reaction space at the same time. Preferably the source chemicals are alternately fed to the reaction space and contacted with the substrate surface, thus providing for ALD type growth of metal carbide on the substrate.

The by-products of the reaction between the surface bound transition metal compound and the carbon source compound are preferably gaseous and thus can easily be removed from the reaction space by varying the reaction space pressure and/or with inert gas flow. Preferably the carbon source compound leaves some carbon in the metal carbide film and takes halogens away from the substrate surface.

While the byproducts of the net reaction $WF_6 + (CH_3CH_2)_3B$ have not been thoroughly analyzed, it is tentatively assumed that if a bond between carbon atoms is broken in the triethyl boron molecule when the molecule is near a tungsten fluoride molecule, some CH_3F will be produced as a byproduct. Also it is tentatively assumed that if a bond between boron and carbon in the triethyl boron molecule is broken when the molecule is near a tungsten fluoride molecule, some CH_3CH_2F and BF_3 will be produced as gas phase byproducts. However, the present invention is not limited to these tentative assumptions.

It is also possible that the carbon source chemical can change the oxidation state of the surface bound transition metal compound molecules. Analyses of thin films of the present invention revealed a high metal-to-carbon ratio W_3C in the carbide thin film. This indicates a partial reduction of tungsten on the surface.

In one embodiment inert gas flow dilutes the byproducts of the reaction between the carbon source compound and the surface bound transition metal compound until the concentration of the gas phase byproducts is insignificant in the reaction space.

Preferably the carbon source compound leaves carbon in the growing transition metal carbide thin film. When a transition metal halide is used as a metal source compound, a halide byproduct may be formed in the reaction with the carbon source compound. For example, if a boron carbon source is used, a boron halide may be formed as a byproduct. The examples in Table 1 show that the resulting boron halides are volatile at a preferred substrate temperature, for example 350 °C, and that they will not condense on the substrate surface. The volatility allows them to be removed from the reaction space as described above.

Boiling point temperatures in Tables 1 to 5 indicate that the vapor pressure of the compound is 1013 mbar (760 torr). However, much lower vapor pressures, down to about 0.01 to 0.1 mbar are sufficient for ALD processes.

TABLE 1

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The following chart is derived from information in N. N. Greenwood and A. Earnshaw, "Chemistry of Elements, 1st ed., Pergamon Press, Oxford, England 1986, p. 220, 225.

Examples of Boron Halides

	Compound	Melting point [°C]	Boiling point [°C]
15	BF3	-127.1	-99.9
	BCI3	-107	+12.5
	BBr ₃	-46	+91.3
	Bl3	+49.9	+210
	B ₂ F ₄	-56	-34
20	B ₂ Cl ₄	-92.6	+65.5

Similarly, halogenated hydrocarbons have high volatility (Table 2) at a preferred substrate temperature, for example $350\,^{\circ}$ C.

TABLE 2.

Examples of Alkyl Halides

The following chart is derived from information contained in CRC Handbook of Chemistry and Physics, 61st ed., Editor: R. C. Weast, CRC Press, Florida, USA 1981.

5	Compound	Melting point [°C]	Boiling point [°C]
	Methyl fluoride, CH ₃ F	-141.8	·78.4
	Methyl chloride, CH3Cl	.97.1	-24.2
	Methyl bromide, CH3Br	-93.6	+3.6
	Methyl iodide, CH ₃ I	-66.4	+42.4
0	Tetrafluoro methane, CF ₄	-150	-129
	Tetrachloro methane, CCl ₄	.23	+76.5
	Ethyl fluoride, CH ₃ CH ₂ F	-143.2	-37.7
	Ethyl chloride, CH3CH2Cl	-136.4	+12.3
	Ethyl bromide, CH3CH2Br	-118.6	+38.4
15	Ethyl iodide, CH3CH2I	-108	+72.3

Tables 3 and 4 show that byproducts consisting of silicon or phosphorus halides also have high vapor pressure, making it possible to utilize reactive organic silicon and phosphorus compounds as carbon sources for the metal carbide deposition.

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TABLE 3

Examples of Silicon Halides

CRC Handbook of Chemistry and Physics, 61st ed., Editor: R. C. Weast, CRC Press, Florida, USA 1981, pp. B-142 - B-143)

Compound	Melting point [°C]	Boiling point (°C)
SiF ₄	·90.2	-86
SiCl ₄	-70	+57.6
SiBr ₄	+5.4	+ 154
Sil ₄	+ 120.5	+ 287.5
Si ₂ Cl ₆	-1	+145
SiCl ₂ F ₂	-144	-31.7
SiCIF ₃	-138	-70
SiBr ₂ Cl ₂	-45.5	104
	SiF ₄ SiCl ₄ SiBr ₄ Sil ₄ Si ₂ Cl ₆ SiCl ₂ F ₂ SiClF ₃	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

TABLE 4

Examples of Phosphorus Halides

The following chart is derived from information contained in N. N. Greenwood and A. Earnshaw, "Chemistry of Elements, 1st ed., Pergamon Press, Oxford, England 1986, p. 568, 572.

5	Compound	Melting point [°C]	Boiling point [°C]
	PF3	-151.5	-101.8
	PCI3	-93.6	+76.1
	PBr ₃	-41.5	+173.2
	Pl ₃	+61.2	
10	P ₂ F ₄	-86.5	-6.2
	P ₂ Cl ₄	-28	
	P_2I_4	+125.5	
	PF ₅	-93.7	-84.5
	PCI ₅	+167	+ 160 (subl.)
15	PI ₅	+41	
	PCI4F	-59	+67
	PCI ₂ F ₃	_. -125	+7.1
	PCIF ₄	-132	-43.4

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TABLE 5

Examples of Commercial Carbon Source Chemicals from Sigma Aldrich

Carbon sources that are useful for the metal carbide depositions disclosed herein and that are commercially available include:

	Compound	<u>Synonym</u>	Boiling point
25	Triethylborane (CH ₃ CH ₂) ₃ B	triethylboron	+95
	Tetraethylsilane (CH ₃ CH ₂) ₄ Si	tetraethylsilicon	+ 153
	Tetramethylsilane (CH ₃) ₄ Si	tetramethylsilicon	+27
	Triethylphosphine (CH3CH2)3P	triethylphosphor	+127

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EXAMPLE 1

The deposition of tungsten carbide from WF₆ and (CH₂CH₂)₃B

Tungsten hexaftuoride WF₆ was used as the metal source chemical and triethyl boron $(CH_3CH_2)_3B$ was used as the carbon source to produce a transition metal carbide thin film on a substrate.

A silicon wafer was loaded into the reaction space of a Pulsar™ 2000 reactor, commercially available from ASM Microchemistry Oy of Espoo, Finland, which is designed for ALD processes. The reaction space was evacuated

with a mechanical vacuum pump. After evacuation the pressure of the reaction space was adjusted to about 5 mbar · 10 mbar (absolute) with flowing nitrogen gas that had a purity of 99.9999%. Then the reaction space was allowed to stabilize at about 350°C. Alternating pulses of electronic grade WF₆ and (CH₃CH₂)₃B were vaporized from external sources, introduced into the reaction space and contacted with the substrate surface. The source compound pulses were separated from each other by purging with flowing nitrogen gas. The pulsing cycle consisted of the two source compound pulses and the two nitrogen purges. The pulsing cycle was repeated 167 times.

The pulsing and purging times of the pulsing cycle were as follows:

	WF ₆ pulse	0.25 s
	N₂ purge	3.0 s
10	(CH ₃ CH ₂) ₃ B pulse	0.5 s
	N₂ purge	3.0 s

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Optimization of the process conditions shortens the purging times relative to the above-described cycle.

After the deposition process, the silicon substrate was unloaded from the reactor for inspection and analysis. The thin film covered the whole top surface of the substrate and it had a metallic luster and gray color. It had good adhesion to the wafer and was electrically conductive. Thin film samples were analyzed with TOF-ERDA (Time-Of-Flight Elastic Recoil Detection Analysis) for elements, with EDS (Electron Diffraction Spectroscopy) for thin film thickness and with four-point probe for sheet resistance. Resistivity was calculated from the thickness and sheet resistance values.

According to TOF-ERDA, the thin film samples consisted of tungsten and carbon in an atomic ratio corresponding to W_3C . The thickness of the samples was about 23 nm, indicating that the growth rate of the tungsten carbide film had been about 1.4 Å/cycle. This value is below the lattice constant of tungsten carbide, possibly due to the molecular size of the precursors that occupy more of the substrate surface than tungsten and carbon atoms do. The resistivity of the film was in the range of 200 micro-ohm-cm. The films had only about 1.0 atomic % - 1.5 atomic % of fluorine as an impurity.

Example 2

General description of the metal carbide film deposition process

A substrate is placed into a reaction space. The reaction space is adjusted to a preferred temperature and the gas atmosphere of the reaction space is adjusted to a preferred pressure. A repeatable process sequence consisting of four basic steps is then begun. A vapor phase pulse of a transition metal source compound is introduced to the reaction space and contacted with the substrate surface. After a first contact time the surplus transition metal source compound and any reaction byproducts are removed from the reaction space by varying the reaction space pressure and/or by inert gas flow. After the first purging time a vapor phase pulse of a carbon source compound is introduced to the reaction chamber and contacted with the substrate surface. After a second contact time the surplus carbon source compound and any reaction byproducts are removed from the reaction space by varying the reaction space pressure and/or by inert gas flow. After the second purging time the process sequence may be repeated until a

metal carbide thin film of a specified thickness is obtained. Finally, the substrate having a thin film is transported from the reaction chamber.

The carbon source compound may be a boron, silicon or phosphorus carbon source compound.

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EXAMPLE 3

ALD metal carbides as diffusion barriers for integrated circuits

A substrate, as shown in Figure 1, having trench 1 and via 2 openings, etch stop layers 3, via insulator 4 and trench insulator 5 is placed in the reaction space of an ALD reactor. The reaction space is evacuated to vacuum and the pressure of the reaction space is adjusted to a preferred pressure with an inert gas, preferably nitrogen. A preferred pressure is in the range of about 1 mbar to 50 mbar, more preferably about 3 mbar to 10 mbar. The temperature of the reaction space is then stabilized at the preferred process temperature. The temperature is preferably in the range of 300°C to 425°C, more preferably in the range of about 325°C to 375°C, and is most preferably set at about 350°C. A transition metal carbide layer 6 is then produced on the substrate by the following cycle:

a transition metal source compound is introduced into the reaction space and contacted with the substrate for a first pulse time;

surplus transition metal source compound molecules and any byproduct molecules are removed from the reaction space during the first purge time;

a carbon source compound is introduced to the reaction space and contacted with the substrate for a second pulse time;

surplus carbon source compound molecules and any byproduct molecules are removed from the reaction space during the second purge time.

The transition metal source compound is preferably selected from the group consisting of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W compounds. Metal halide compounds are more preferred. The carbon source compound is selected from the group consisting of boron, silicon and phosphorus compounds that contain carbon. Alkyl borons, alkyl silicons and alkyl phosphorus compounds are more preferred.

Ouring the purge time, inert or noble gas is introduced to the reaction space to dilute the surplus compound and byproduct concentration to an insignificant level by forcing these molecules to enter the pumping line.

Each pulsing cycle increases the thickness of the film by up to one molecular layer of metal carbide. The exact number of the pulsing cycles depends on the application and the desired thickness of the film.

The transition metal carbide layer may serve as a diffusion barrier. The substrate may then be further manipulated, such as by the deposition of a metal seed layer.

EXAMPLE 4

Coating tools with metal carbide in a batch process

It would be beneficial to provide bits for drilling that have an extended useful life. This may be achieved by coating them with a metal carbide. Because the ALD type process of the present invention is not sensitive to the

sample geometry, a batch process can be used. Thus, parts to be coated may be relatively small. The ability to use a batch process also decreases the coating costs per part significantly.

A number of bits are set in a substrate holder that is then loaded into the reaction space of a batch reactor. The reaction space is evacuated to vacuum. The pressure of the reaction space is adjusted to a preferred pressure with an inert gas, preferably nitrogen. A preferred pressure is in the range of about 1 mbar to 50 mbar, more preferably about 3 mbar to 10 mbar. The temperature of the reaction space is then stabilized at the preferred process temperature. The temperature is preferably in the range of about 300°C to 425°C, more preferably in the range of about 325°C to 375°C, and in the illustrated embodiment is set at about 350°C.

The transition metal carbide deposition process consists of the following repeatable process steps that form a pulsing cycle:

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a transition metal source compound is introduced into the reaction space and contacted with the substrates for a first pulse time;

surplus transition metal source compound molecules and any byproduct molecules are removed from the reaction space during a first purge time;

a carbon source compound is introduced to the reaction space and contacted with the substrates for a second pulse time;

surplus carbon source compound molecules and any byproduct molecules are removed from the reaction space during a second purge time.

The transition metal source compound is preferably selected from the group consisting of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W compounds. Metal halide compounds are more preferred. The carbon source chemical is selected from the group consisting of volatile boron, silicon and phosphorus compounds that contain carbon. Alkyl borons, alkyl silicons and alkyl phosphorus compounds are more preferred.

During the purge time, inert or noble gas is introduced to the reaction space to dilute the surplus compound and byproduct concentration to an insignificant level by forcing these molecules to enter the pumping line.

Each pulsing cycle increases the thickness of the film by up to one molecular layer of metal carbide. The exact number of the pulsing cycles depends on the application and the desired thickness of the film.

EXAMPLE 5

ALD grown metal carbide as a starting surface for diamond deposition

Metal carbide thin films may serve as a nucleation surface for the growth of diamond thin film. Metal carbide thin films are deposited on a substrate by the ALD type process of the present invention. The metal carbide thin film may then be used as a starting layer for the subsequent deposition of diamond thin film on the substrate.

EXAMPLE 6

Electrical contacts to SiC with the help of ALD metal carbides

In order to improve the process of making electrical contacts to a silicon carbide surface, an intermediate layer consisting of a metal carbide thin film is produced by the ALD type process of the present invention. A silicon

carbide substrate is provided. The substrate surface has enough reactive sites for the nucleation of the first few metal carbide molecular layers. The most critical part of the process is the adsorption of the first molecular layer of the ALD source chemical on the silicon carbide surface. The deposition process can be started either with the metal source chemical or the carbon source chemical.

EXAMPLE 7

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ALD metal carbides as an adhesion layer

Metal carbide thin films may be used as an intermediate layer on a substrate to improve the adhesion of a subsequent material layer deposited on the substrate. The metal carbide thin film is produced according to the deposition process described above.

EXAMPLE 8

Deposition of metal carbides in an ALD process with plasma

Adding pulsed plasma to the deposition process of the present invention allows for the use of a lower deposition temperature. It also makes it possible to use fragments of organic compounds in the form of radicals for the deposition of metal carbide thin film by an ALD type process.

In this embodiment, a substrate is first placed in the reaction space. The pressure of the reaction space is set to a preferred pressure with a vacuum pump and flowing inert gas. The temperature of the reaction space is set to a preferred temperature and the deposition process is started.

The deposition process comprises the following repeatable pulse and purge steps that form the basic deposition cycle:

metal source compound is introduced into the reaction chamber and contacted with the substrate for a first pulse time;

surplus metal source compound molecules and any byproduct molecules are removed from the reaction space during a first purge time;

carbon source compound is introduced into the reaction chamber in the form of plasma radicals and contacted with the substrate for a second pulse time;

surplus carbon source compound molecules and any byproduct molecules are removed from the reaction space during a second purge time.

The maximum deposition rate of the metal carbide thin film that allows for controlled thickness uniformity is one molecular layer per cycle. The carbon source compound is preferably an organic compound that contains only carbon and hydrogen. The carbon source compound is preferably turned into plasma with UV radiation, electric arc, RF generator or any other method known in the art that is capable of forming plasma from gas atoms or molecules. The resulting radicals preferably have a high hydrogen/carbon ratio, thus improving the volatility of these species and decreasing the possibility of obtaining a low-volatility carbon-rich coating on the substrate. Because this embodiment utilizes pulsed plasma, it is preferable to switch off or redirect the plasma source during the metal source compound pulse to avoid uncontrolled deposition of metal on the substrates.

The cycle may be repeated as many times as necessary to produce a film of the desired thickness. After the deposition process the substrate is unloaded from the reaction space.

EXAMPLE 9

ALD deposition of metal carbides for catalysts

Substrate material is loaded to a substrate holder. In the case of powders having high area/volume ratio, the substrate holder consists of a length of container having a sinter on both ends. The substrate holder may be placed horizontally in the reaction space. In this orientation the substrate holder is filled with substrate powder so that there is no free gas space inside the substrate holder. In this orientation the source compound gases and purging gas preferably go through the powder. The substrate holder may alternatively be placed vertically in the reaction space. In this orientation there may be some free gas space left inside the substrate holder so that the substrate powder can float in the gas stream that preferably comes through the bottom sinter and exits through the top sinter.

Transition metal carbide is deposited on the substrate surface by the ALD type process described above. However, in this embodiment source compound gases are preferably directed through the container holding the powder, thus ensuring that the gas contacts the particles of the powder. Due to the large surface area to be coated the pulse and purge times are preferably extended compared to the values provided for non-powder substrates.

EXAMPLE 10

ALD metal carbides as corrosion protection

Bearings are an example of parts that may benefit from a hard, protective outer layer when used in corroding atmospheres. A set of bearings is loaded into a perforated substrate holder. The holes on the substrate holder have a conical opening at the upper surface of the holder. The bearings rest on the bottom of these shallow cones. The substrate holder is transported into the reaction space where it is connected to the source gas and inert gas lines. The reaction space is evacuated to vacuum. The pressure of the reaction chamber is adjusted with flowing inert gas to the preferred processing pressure. Inert gas enters the reaction chamber through the holes of the substrate holder and raises the bearings from the bottom of the cones. The bearings preferably rotate freely in the flowing nitrogen streams (Bernoulli's principle) and they are not in contact with any solid surface during the deposition process. The temperature of the reaction space is adjusted to the preferred deposition temperature.

The ALD type metal carbide deposition process is started and comprises the following steps:

metal source compound is introduced to the reaction space and contacted with the substrates for a first pulse time;

surplus metal source compound molecules and any byproduct molecules are removed from the reaction space during a first purge time;

carbon source compound is introduced to the reaction space and contacted with the substrates for a second pulse time;

surplus carbon source compound molecules and any byproduct molecules are removed from the reaction space during a second purge time.

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Source chemical gases flow through the conical holes of the substrate holder and contact the bearings that are held in the vertical gas streams. The process forms up to a molecular layer of metal carbide per pulsing cycle. After the deposition process, nitrogen flow is slowly decreased until the bearings have returned to the bottom of the cones. The substrate holder may be unloaded through a load lock or the pressure of the reaction chamber may be increased to the external room pressure with inert gas and the substrate holder unloaded without the use of a load lock chamber.

WE CLAIM:

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- A method of depositing a transition metal carbide thin film by an atomic layer deposition (ALD) process.
- The method of Claim 1, wherein vapor-phase pulses are alternately introduced in a cycle
 comprising:

introducing a transition metal source gas into a reaction space containing a substrate;

removing excess transition metal source gas and gaseous reaction byproducts from the reaction

space;

introducing a carbon source gas into the reaction space; and

removing excess carbon source gas and gaseous reaction byproducts from the reaction space.

- 3. The method of Claim 2, wherein the metal source gas reacts with a surface of the substrate, thereby producing a surface bound transition metal complex.
- 4. The method of Claim 3, wherein the surface bound transition metal complex forms no more than about one monolayer.
- 15 5. The method of Claim 3, wherein the carbon source gas reacts with the surface bound transition metal complex to leave a transition metal carbide.
 - 6. The method of Claim 5, wherein gaseous reaction byproducts are formed by the reaction of the surface bound transition metal complex with the carbon source gas.
 - 7. The method of Claim 2, wherein the transition metal source gas and carbon source gas are each fed into the reaction space with the aid of an inert carrier gas.
 - 8. The method of Claim 2, further comprising feeding an inert gas pulse to the reaction space after each pulse of transition metal source gas and carbon source gas.
 - 9. The method of Claim 2, wherein the transition metal source gas comprises a metal selected from the group consisting of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W.
 - 10. The method of Claim 9, wherein the transition metal source gas is a metal halide.
 - The method of Claim 10, wherein the transition metal source gas is tungsten hexafluoride.
 - 12. The method of Claim 2, wherein the carbon source gas comprises a boron compound comprising at least one boron atom and at least one carbon atom.
 - 13. The method of Claim 12, wherein the boron source compound is an alkyl boron compound.
- 30 14. The method of Claim 13, wherein the boron compound is triethylboron.
 - 15. The method of Claim 2, wherein the carbon source gas comprises a silicon compound comprising at least one silicon atom and at least one carbon atom.
 - 16. The method of Claim 15, wherein the silicon source compound is an alkylsilicon compound.
 - 17. The method of Claim 2, wherein the carbon source gas comprises a phosphorous compound comprising at least one phosphorous atom and at least one carbon atom.

18. The method of Claim 17, wherein the phosphorous source compound is an alkylphosphorus compound.

- 19. The method of Claim 2, wherein the carbon source gas comprises a hydrocarbon.
- 20. The method of Claim 19, wherein the hydrocarbon is a linear or branched alkane.
- 5 21. The method of Claim 19, wherein the carbon source gas comprises radicals generated in a plasma formed from hydrocarbons.
 - 22. The method of Claim 1, wherein the transition metal carbide thin film forms a conductive diffusion barrier in an integrated circuit.
- 23. The method of Claim 22, wherein the conductive diffusion barrier comprises a liner in a dual damascene void.
 - 24. The method of Claim 1, wherein the transition metal carbide thin film forms a hard coating on a substrate to protect against mechanical wear.
 - 25. The method of Claim 1, wherein the transition metal carbide thin film forms a corrosion protection layer.
- 15 26. The method of Claim 1, wherein the transition metal carbide thin film forms a chemical reaction catalyst.
 - A method of producing an electron conductor in an integrated circuit by an atomic layer deposition (ALD) process, in which each of a plurality of cycles comprises exposing an adsorbed metal complex on a substrate to a carbon compound, the carbon compound reacting with the adsorbed metal complex to form no more than about one monolayer of metal carbide.
 - 28. The method of Claim 27, wherein at least a portion of the metal source gas adsorbs upon the substrate, thereby producing the adsorbed metal complex.

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29. The method of Claim 27, wherein the metal complex comprises a metal selected from the group consisting of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W.

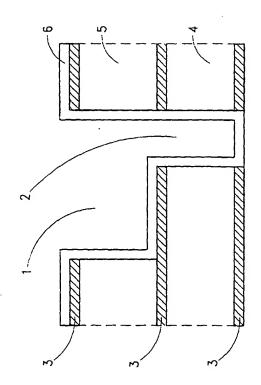


FIG. 1

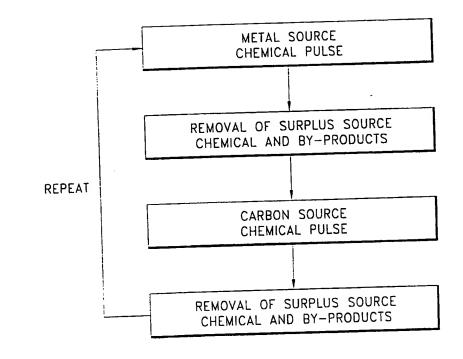


FIG. 2

INTERNATIONAL SEARCH REPORT Int. ional Application No

PCT/US 00/28537

A. CLASSII IPC 7	FICATION OF SUBJECT MATTER C23C16/32 H01L21/00								
According to International Patent Classification (IPC) or to both national classification and IPC									
	SEARCHED	Variation and the second secon							
IPC 7	cumentation searched (classification system followed by classificat C30B C23C H01L	ion symbols)							
Documentat	ion searched other than minimum documentation to the extent that	such documents are included in the fields so	earched						
	ata base consulted during the international search (name of data ba)						
C. DOCUM	ENTS CONSIDERED TO BE RELEVANT								
Category °	Citation of document, with indication, where appropriate, of the re	elevant passages	Relevant to claim No.						
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Α	WO 96 18756 A (NKT RES CENTER AS KRISTIAN (DK); PRYDS NINI HAMAWI 20 June 1996 (1996-06-20) page 4, line 15 -page 7, line 34 III	(DK)) ·	. 1-29						
Furt	her documents are listed in the continuation of box C.	X Patent family members are listed	in annex.						
Special categories of cited documents: 'A' document defining the general state of the art which is not considered to be of particular relevance 'E' earlier document but published on or after the international filing date 'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) 'I' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone 'Y' document of particular relevance; the claimed invention involve an inventive step when the document is taken alone 'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the									
O document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filling date but later than the priority date claimed *B* document published prior to the international filling date but later than the priority date claimed *B* document member of the same patent family									
	actual completion of the International search	Date of mailing of the international sea							
3	1 January 2001	07/02/2001							
Name and r	mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk	Authorized officer							
	Tel. (+31-70) 340-3016 Fax: (+31-70) 340-3016	Ekhult, H	!						

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inti Jonal Application No PCT/US 00/28537

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Basic Patent (Number, Kind, Date): FI 200000564 A0 20000310

Patent Family:

Patent Number	Kind	Date	Application Number	Kind	Date
AU 200068003	A 5	20010319	AU 200068003	Α	20000824
AU 200079257	A5	20010423	AU 200079257	Α	20001012
AU 200079268	A5	20010423	AU 200079268	Α	20001013
AU 200110884	A5	20010430	AU 200110884	Α	20001016
AU 200112082	A5	20010430	AU 200112082	A	20001016
FI 9902233	Α	20010416	FI 992233	A	19991015
FI 9902234	A	20010416	FI 992234	A	19991015
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FI 200000564	Α	20010416	FI 2000564	Α	20000310
FI 200000564	A0	20000310	FI 2000564	Α	20000310 (Basic)
WO 200115220	A1	20010301	WO 2000US23252	Α	20000824
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WO 200129891	A1	20010426	WO 2000US23213	Α	20000824
WO 200129893	A1	20010426	WO 2000US28654	A	20001016

Priority Data:

Patent Number	Kind	Date
US 150486	P	19990824
US 159799	P	19991015
US 176944	P	20000118
WO 2000US23252	W	20000824
FI 992233	Α	19991015
WO 2000FI884	W	20001012
FI 992234	A	19991015
WO 2000FI895	W	20001013
FI 992235	Α	19991015
FI 2000564	Α	20000310
US 176948	P	20000118
WO 2000US28537	W	20001016
US 175799	P	19991015

PATENT FAMILY:

Australia (AU)

Patent (Number, Kind, Date): AU 200068003 A5 20010319

METHOD FOR BOTTOMLESS DEPOSITION OF BARRIER LAYERS IN INTEGRATED CIRCUIT

METALLIZATION SCHEMES (English)

Patent Assignee: ASM INC

Author (Inventor): SATTA ALESSANDRA; MAEX KAREN; ELERS KAI-ERIK; SAANILA VILLE

ANTERO; SOININEN PEKKA JUHA; HAUKKA SUVI P

Priority (Number, Kind, Date): US 150486 P 19990824; US 159799 P 19991015; US 176944 P

20000118; WO 2000US23252 W 20000824

Applic (Number, Kind, Date): AU 200068003 A 20000824

IPC: * H01L-021/768; H01L-023/532; H01L-021/285; C23C-016/00

CA Abstract No: * 134(13)187114R; 134(21)304079W; 134(22)318948R

Derwent WPI Acc No: * C 01-218475

Language of Document: English

Patent (Number, Kind, Date): AU 200079257 A5 20010423

METHOD OF MODIFYING SOURCE CHEMICALS IN AN ALD PROCESS (English)

Patent Assignee: ASM MICROCHEMISTRY OY

Author (Inventor): ELERS KAI-ERIK

Priority (Number, Kind, Date): FI 992233 A 19991015; WO 2000FI884 W 20001012

Applic (Number, Kind, Date): AU 200079257 A 20001012 IPC: * C23C-016/44; C23C-016/00; C30B-025/02; C30B-035/00

CA Abstract No: * 134(21)303341P; 134(21)304215N; 134(22)318948R

Language of Document: English

Patent (Number, Kind, Date): AU 200079268 A5 20010423

METHOD OF DEPOSITING TRANSITION METAL NITRIDE THIN FILMS (English)

Patent Assignee: ASM MICROCHEMISTRY OY

Author (Inventor): ELERS KAI-ERIK; HAUKKA SUVI PAIVIKKI; SAANILA VILLE ANTERO;

KAIPIO SARI JOHANNA; SOININEN PEKKA JUHA

Priority (Number, Kind, Date): FI 992234 A 19991015; WO 2000FI895 W 20001013

Applic (Number, Kind, Date): AU 200079268 A 20001013

IPC: * C23C-016/44; C23C-016/00; C30B-025/02; H05K-003/00

CA Abstract No: * 134(21)303342Q; 134(21)304215N; 134(22)318948R

Language of Document: English

Patent (Number, Kind, Date): AU 200110884 A5 20010430

DEPOSITION OF TRANSITION METAL CARBIDES (English)

Patent Assignee: ASM INC

Author (Inventor): ELERS KAI-ERIK; HAUKKA SUVI P; SAANILA VILLE ANTERO; KAIPIO SARI

JOHANNA; SOININEN PEKKA JUHA

Priority (Number, Kind, Date): FI 992233 A 19991015; FI 992234 A 19991015; FI 992235 A 19991015; FI 2000564 A 20000310; US 159799 P 19991015; US 176948 P 20000118; WO

2000US28537 W 20001016

Applic (Number, Kind, Date): AU 200110884 A 20001016

IPC: * C23C-016/32; H01L-021/00

CA Abstract No: * 134(13)187114R; 134(21)303341P; 134(21)303342Q; 134(21)304079W; 134(21)

304215N; 134(22)318948R

Derwent WPI Acc No: * C 01-218475; C 01-308262; C 01-308263

Language of Document: English

Patent (Number, Kind, Date): AU 200112082 A5 20010430

METHOD FOR DEPOSITING NANOLAMINATE THIN FILMS ON SENSITIVE SURFACES (English)

Patent Assignee: ASM INC

Author (Inventor): ELERS KAI-ERIK; HAUKKA SUVI P; SAANILA VILLE ANTERO; KAIPIO SARI

JOHANNA; SOININEN PEKKA JUHA

Priority (Number, Kind, Date): FI 992233 A 19991015; FI 992234 A 19991015; FI 992235 A 19991015; FI 2000564 A 20000310; US 175799 P 19991015; US 176948 P 20000118; WO 2000US28654 W 20001016

Applic (Number, Kind, Date): AU 200112082 A 20001016

IPC: * H01L-021/768; H01L-021/285; C23C-016/00

CA Abstract No: * 134(21)303341P; 134(21)303342O; 134(21)304215N; 134(22)318948R

Derwent WPI Acc No: * C 01-308262; C 01-308263

Language of Document: English

Finland (FI)

Patent (Number, Kind, Date): FI 9902233 A 20010416

MENETELMAE LAEHDEKEMIKAALIEN MUUNTAMISEKSI ALCVD-PROSESSISSA FOERFARANDE FOER MODIFIERING AV UTGAANGSAEMNESKEMIKALIERNA I EN ALCVD-PROSESS (Swedish)

Patent Assignee: ASM MICROCHEMISTRY LTD (FI)

Author (Inventor): ELERS KAI-ERIK (FI)

Priority (Number, Kind, Date): FI 992233 A 19991015 Applic (Number, Kind, Date): FI 992233 A 19991015

IPC: * C23C-016/44

Language of Document: Finnish; Swedish

Patent (Number, Kind, Date): FI 9902234 A 20010416

MENETELMAE SIIRTYMAEMETALLINITRIDIOHUTKALVOJEN KERROSTAMISEKSI FOERFARANDE FOER FRAMSTAELLNING AV OEVERGAANGSMETALLNITRIDTUNNFILMER (Swedish)

Patent Assignee: ASM MICROCHEMISTRY LTD (FI)

Author (Inventor): ELERS KAI-ERIK (FI); HAUKKA SUVI (FI); SAANILA VILLE (FI); KAIPIO SARI (FI); SOININEN PEKKA (FI)

Priority (Number, Kind, Date): FI 992234 A 19991015 Applic (Number, Kind, Date): FI 992234 A 19991015

IPC: * C23C-016/44; C30B-025/02

Language of Document: Finnish; Swedish

Patent (Number, Kind, Date): FI 9902235 A 20010416

MENETELMAE ALKUAINEOHUTKALVOJEN KASVATTAMISEKSI FOERFARANDE FOER FRAMSTAELLNING AV ELEMENTTUNNFILMER (Swedish)

Patent Assignee: ASM MICROCHEMISTRY LTD (FI)

Author (Inventor): ELERS KAI-ERIK (FI); SAANILA VILLE (FI); KAIPIO SARI (FI); SOININEN PEKKA (FI)

Priority (Number, Kind, Date): FI 992235 A 19991015 Applic (Number, Kind, Date): FI 992235 A 19991015

IPC: * C23C-016/44; C30B-025/02

Language of Document: Finnish: Swedish

Patent (Number, Kind, Date): FI 200000564 A 20010416

MENETELMAE NANOLAMINAATTIEN VALMISTAMISEKSI FOERFARANDE FOER

FRAMSTAELLNING AV NANOLAMINATER (Swedish)

Patent Assignee: ASM MICROCHEMISTRY OY (FI)

Author (Inventor): ELERS KAI-ERIK (FI); SAANILA VILLE (FI); KAIPIO SARI (FI); SOININEN PEKKA (FI)

Priority (Number, Kind, Date): FI 2000564 A 20000310; FI 992233 A 19991015; FI 992234 A

19991015; FI 992235 A 19991015

Applic (Number, Kind, Date): FI 2000564 A 20000310

IPC: * C23C-016/30

Language of Document: Finnish; Swedish

Patent (Number, Kind, Date): FI 200000564 A0 20000310

MENETELMAE NANOLAMINAATTIEN VALMISTAMISEKSI FOERFARANDE FOER

FRAMSTAELLNING AV NANOLAMINATER (Swedish)

Patent Assignee: ASM MICROCHEMISTRY OY (FI)

Author (Inventor): ELERS KAI-ERIK (FI); SAANILA ANTERO VILLE (FI); KAIPIO JOHANNA

SARI (FI); SOININEN JUHA PEKKA (FI)

Priority (Number, Kind, Date): FI 2000564 A 20000310; FI 992233 A 19991015; FI 992234 A

19991015; FI 992235 A 19991015

Applic (Number, Kind, Date): FI 2000564 A 20000310

IPC: * C25D

Language of Document: Finnish; Swedish

World Intellectual Property Organization, PCT (WO)

Patent (Number, Kind, Date): WO 200115220 A1 20010301

METHOD FOR BOTTOMLESS DEPOSITION OF BARRIER LAYERS IN INTEGRATED CIRCUIT

METALLIZATION SCHEMES (English)

Patent Assignee: ASM INC (US); SATTA ALESSANDRA (BE); MAEX KAREN (BE); ELERS KAI ERIK (FI); SAANILA VILLE ANTERO (FI); SOININEN PEKKA JUHA (FI); HAUKKA SUVI P (FI) Author (Inventor): SATTA ALESSANDRA (BE); MAEX KAREN (BE); ELERS KAI-ERIK (FI);

SAANILA VILLE ANTERO (FI); SOININEN PEKKA JUHA (FI); HAUKKA SUVI P (FI)

Priority (Number, Kind, Date): US 150486 P 19990824; US 159799 P 19991015; US 176944 P 20000118

Applic (Number, Kind, Date): WO 2000US23252 A 20000824

Designated States: (National) AE; AG; AL; AM; AT; AU; AZ; BA; BB; BG; BR; BY; BZ; CA; CH; CN; CR; CU; CZ; CZ; DE; DE; DK; DK; DM; DZ; EE; EE; ES; FI; FI; GB; GD; GE; GH; GM; HR; HU; ID; IL; IN; IS; JP; KE; KG; KP; KR; KZ; LC; LK; LR; LS; LT; LU; LV; MA; MD; MG; MK; MN; MW; MX; MZ; NO; NZ; PL; PT; RO; RU; SD; SE; SG; SI; SK; SK; SL; TJ; TM; TR; TT; TZ; UA; UG; US; UZ; VN; YU; ZA; ZW (Regional) GH; GM; KE; LS; MW; MZ; SD; SL; SZ; TZ; UG; ZW; AM; AZ; BY; KG; KZ; MD; RU; TJ; TM; AT; BE; CH; CY; DE; DK; ES; FI; FR; GB; GR; IE; IT; LU; MC; NL; PT; SE; BF; BJ; CF; CG; CI; CM; GA; GN; GW; ML; MR; NE; SN; TD; TG

Filing Details: WO 130000 With international search report; Before expiration of time limit for amending the claims and to be republished in the event of the receipt of the amendments

IPC: * H01L-021/768; H01L-023/532; H01L-021/285; C23C-016/00

CA Abstract No: * 134(13)187114R; 134(21)304079W; 134(22)318948R; 134(13)187114R

Derwent WPI Acc No: * C 01-218475; C 01-328500; C 01-328533; C 01-218475

Language of Document: English

Patent (Number, Kind, Date): WO 200127346 A1 20010419

METHOD OF MODIFYING SOURCE CHEMICALS IN AN ALD PROCESS (English)

Patent Assignee: ASM MICROCHEMISTRY OY (FI); ELERS KAI ERIK (FI)

Author (Inventor): ELERS KAI-ERIK (FI)

Priority (Number, Kind, Date): FI 992233 A 19991015

Applic (Number, Kind, Date): WO 2000FI884 A 20001012

Designated States: (National) AE; AG; AL; AM; AT; AT; AU; AZ; BA; BB; BG; BR; BY; BZ; CA; CH; CN; CR; CU; CZ; CZ; DE; DE; DK; DK; DM; DZ; EE; EE; ES; FI; FI; GB; GD; GE; GH; GM; HR; HU; ID; IL; IN; IS; JP; KE; KG; KP; KR; KR; KZ; LC; LK; LR; LS; LT; LU; LV; MA; MD; MG; MK; MN; MW; MX; MZ; NO; NZ; PL; PT; RO; RU; SD; SE; SG; SI; SK; SK; SL; TJ; TM; TR; TT; TZ; UA; UG; US; UZ; VN; YU; ZA; ZW (Regional) GH; GM; KE; LS; MW; MZ; SD; SL; SZ; TZ; UG; ZW; AM; AZ; BY; KG; KZ;

MD; RU; TJ; TM, AT; BE; CH; CY; DE; DK; ES; FI; FR; GB; GR; IE; IT; LU; MC; NL; PT; SE; BF; BJ; CF; CG: CI; CM; GA; GN; GW; ML; MR; NE; SN; TD; TG Filing Details: WO 100000 With international search report IPC: * C23C-016/44; C23C-016/00; C30B-025/02; C30B-035/00 CA Abstract No: * 134(21)303341P; 134(21)304215N; 134(22)318948R; 134(21)303341P Derwent WPI Acc No: * C 01-308262; C 01-328500; C 01-308262 Language of Document: English Patent (Number, Kind, Date): WO 200127347 A1 20010419 METHOD OF DEPOSITING TRANSITION METAL NITRIDE THIN FILMS (English) Patent Assignee: ASM MICROCHEMISTRY OY (FI); ELERS KAI ERIK (FI); HAUKKA SUVI PAEIVIKKI (FI); SAANILA VILLE ANTERO (FI); KAIPIO SARI JOHANNA (FI); SOININEN PEKKA JUHA (FI) Author (Inventor): ELERS KAI-ERIK (FI); HAUKKA SUVI PAEIVIKKI (FI); SAANILA VILLE ANTERO (FI); KAIPIO SARI JOHANNA (FI); SOININEN PEKKA JUHA (FI) Priority (Number, Kind, Date): FI 992234 A 19991015 Applic (Number, Kind, Date): WO 2000F1895 A 20001013 Designated States: (National) AE; AG; AL; AM; AT; AU; AZ; BA; BB; BG; BR; BY; BZ; CA; CH; CN; CR; CU; CZ; CZ; DE; DE; DK; DK; DM; DZ; EE; EE; ES; FI; FI; GB; GD; GE; GH; GM; HR; HU; ID; IL; IN; IS; JP; KE; KG; KP; KR; KR; KZ; LC; LK; LR; LS; LT; LU; LV; MA; MD; MG; MK; MN; MW; MX; MZ; NO; NZ; PL; PT; RO; RU; SD; SE; SG; SI; SK; SK; SL; TJ; TM; TR; TT; TZ; UA; UG; US; UZ; VN; YU; ZA; ZW (Regional) GH; GM; KE; LS; MW; MZ; SD; SL; SZ; TZ; UG; ZW; AM; AZ; BY; KG; KZ; MD; RU; TJ; TM; AT; BE; CH; CY; DE; DK; ES; FI; FR; GB; GR; IE; IT; LU; MC; NL; PT; SE; BF; BJ; CF; CG; CI; CM; GA; GN; GW; ML; MR; NE; SN; TD; TG Filing Details: WO 100000 With international search report IPC: * C23C-016/44; C23C-016/00; C30B-025/02; H05K-003/00 CA Abstract No: * 134(21)303342Q; 134(21)304215N; 134(22)318948R; 134(21)303342Q Derwent WPI Acc No: * C 01-308263; C 01-328500; C 01-308263 Language of Document: English Patent (Number, Kind, Date): WO 200129280 A1 20010426 DEPOSITION OF TRANSITION METAL CARBIDES (English) Patent Assignee: ASM INC (US); ELERS KAI ERIK (FI); HAUKKA SUVI P (FI); SAANILA VILLE ANTERO (FI); KAIPIO SARI JOHANNA (FI); SOININEN PEKKA JUHA (FI) Author (Inventor): ELERS KAI-ERIK (FI); HAUKKA SUVI P (FI); SAANILA VILLE ANTERO (FI); KAIPIO SARI JOHANNA (FI); SOININEN PEKKA JUHA (FI) Priority (Number, Kind, Date): FI 992233 A 19991015; FI 992234 A 19991015; FI 992235 A 19991015; FI 2000564 A 20000310; US 159799 P 19991015; US 176948 P 20000118 Applic (Number, Kind, Date): WO 2000US28537 A 20001016 Designated States: (National) AE; AG; AL; AM; AT; AU; AZ; BA; BB; BG; BR; BY; BZ; CA; CH; CN; CR; CU; CZ; CZ; DE; DE; DK; DK; DM; DZ; EE; EE; ES; FI; FI; GB; GD; GE; GH; GM; HR; HU; ID; IL; IN; IS; JP; KE; KG; KP; KR; KR; KZ; LC; LK; LR; LS; LT; LU; LV; MA; MD; MG; MK; MN; MW; MX; MZ; NO; NZ; PL; PT; RO; RU; SD; SE; SG; SI; SK; SK; SL; TJ; TM; TR; TT; TZ; UA; UG; US; UZ; VN; YU; ZA; ZW (Regional) GH; GM; KE; LS; MW; MZ; SD; SL; SZ; TZ; UG; ZW; AM; AZ; BY; KG; KZ; MD; RU; TJ; TM; AT; BE; CH; CY; DE; DK; ES; FI; FR; GB; GR; IE; IT; LU; MC; NL; PT; SE; BF; BJ; CF; CG; CI; CM; GA; GN; GW; ML; MR; NE; SN; TD; TG Filing Details: WO 100000 With international search report IPC: * C23C-016/32; H01L-021/00 CA Abstract No: ; 134(22)318948R Derwent WPI Acc No: ; C 01-328500 Language of Document: English Patent (Number, Kind, Date): WO 200129891 A1 20010426 CONFORMAL LINING LAYERS FOR DAMASCENE METALLIZATION (English)

Patent Assignee: ASM INC (US)

Author (Inventor): RAAIJMAKERS IVO; HAUKKA SUVI P; GRANNEMAN ERNST H A; SAANILA

VILLE ANTERO; SOININEN PEKKA JUHA; ELERS KAI-ERIK

Priority (Number, Kind, Date): US 159799 P 19991015; US 176944 P 20000118

Applic (Number, Kind, Date): WO 2000US23213 A 20000824

Designated States: (National) JP; KR (Regional) AT; BE; CH; CY; DE; DK; ES; FI; FR; GB; GR; IE; IT; LU; MC; NL; PT; SE

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CA Abstract No: ; 134(21)304079W Derwent WPI Acc No: ; C 01-328533 Language of Document: English

Patent (Number, Kind, Date): WO 200129893 A1 20010426

METHOD FOR DEPOSITING NANOLAMINATE THIN FILMS ON SENSITIVE SURFACES (English) Patent Assignee: ASM INC (US); ELERS KAI ERIK (FI); HAUKKA SUVI P (FI); SAANILA VILLE

ANTERO (FI): KAIPIO SARI JOHANNA (FI): SOININEN PEKKA JUHA (FI)

Author (Inventor): ELERS KAI-ERIK (FI); HAUKKA SUVI P (FI); SAANILA VILLE ANTERO (FI);

KAIPIO SARI JOHANNA (FI); SOININEN PEKKA JUHA (FI)

Priority (Number, Kind, Date): FI 992233 A 19991015; FI 992234 A 19991015; FI 992235 A

19991015; FI 2000564 A 20000310; US 175799 P 19991015; US 176948 P 20000118

Applic (Number, Kind, Date): WO 2000US28654 A 20001016

Designated States: (National) AE; AG; AL; AM; AT; AT; AU; AZ; BA; BB; BG; BR; BY; BZ; CA; CH; CN; CR; CU; CZ; CZ; DE; DE; DK; DK; DM; DZ; EE; EE; ES; FI; FI; GB; GD; GE; GH; GM; HR; HU; ID; IL; IN; IS; JP; KE; KG; KP; KR; KR; KZ; LC; LK; LR; LS; LT; LU; LV; MA; MD; MG; MK; MN; MW; MX; MZ; NO; NZ; PL; PT; RO; RU; SD; SE; SG; SI; SK; SK; SL; TJ; TM; TR; TT; TZ; UA; UG; US; UZ; VN; YU; ZA; ZW (Regional) GH; GM; KE; LS; MW; MZ; SD; SL; SZ; TZ; UG; ZW; AM; AZ; BY; KG; KZ; MD; RU; TJ; TM; AT; BE; CH; CY; DE; DK; ES; FI; FR; GB; GR; IE; IT; LU; MC; NL; PT; SE; BF; BJ; CF; CG; CI; CM; GA; GN; GW; ML; MR; NE; SN; TD; TG

Filing Details: WO 130000 With international search report; Before expiration of time limit for amending the claims and to be republished in the event of the receipt of the amendments

IPC: * H01L-021/768; H01L-021/285; C23C-016/00

CA Abstract No: * 134(21)303341P; 134(21)303342Q; 134(21)304215N; 134(22)318948R; 134(21) 304215N

Derwent WPI Acc No: * C 01-308262; C 01-308263; C 01-328500

Language of Document: English

World Intellectual Property Organization, PCT (WO) - Legal Status

	Number	Type	Date	Code	Text	
	WO	P	19990824	WO	PRIORITY CLAIMED	
	200115220			AA		
					US 150486 P 19990824	
	WO	P	19991015	WO	PRIORITY CLAIMED	
	200115220			AA		
					US 159799 P 19991015	
	WO	P	20000118	WO	PRIORITY CLAIMED	
	200115220			AA		
					US 176944 P 20000118	
)	WO	P	20000824	WO	APPLICATION DATA	(APPL. DATA)
	200115220			AE		

•					WO 2000US23252 A 20000824	
\bigcirc	WO 200115220	P	20010301	WO AK	DESIGNATED STATES CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED STATES CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
					AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH CN CR CU CZ CZ DE DE DK DK DM DZ EE EE ES FI FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ PL PT RO RU SD SE SG SI SK SK SL TJ TM TR TT TZ UA UG US UZ VN YU ZA ZW	
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					GH GM KE LS MW MZ SD SL SZ TZ UG ZW AM AZ BY KG KZ MD RU TJ TM AT BE CH CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG	
	WO 200115220	P	20010301	WO A1	PUBLICATION OF THE INTERNATIONAL APPLICATION WITH THE INTERNATIONAL SEARCH REPORT	(PUB. OF THE INTERNATIONAL APPL. WITH THE INTERNATIONAL SEARCH REPORT)
	WO 200115220	P	20010425	WO 121	EP: THE EPO HAS BEEN INFORMED BY WIPO THAT EP WAS DESIGNATED IN THIS APPLICATION	
	WO 200115220	P	20010531	DFPE	REQUEST FOR PRELIMINARY EXAMINATION FILED PRIOR TO EXPIRATION OF 19TH MONTH FROM PRIORITY DATE	
	WO 200127346	P	19991015	WO AA	PRIORITY (PATENT)	
					FI 992233 A 19991015	
	WO 200127346	P	20001012	WO AE	APPLICATION DATA	(APPL. DATA)
					WO 2000FI884 A 20001012	
	WO 200127346	P	20010419		DESIGNATED STATES CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED STATES CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
_)					AE AG AL AM AT AT AU AZ BA BB BG BR BY BZ CA CH CN CR CU CZ CZ DE	,

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	WO 200127346	P	20010419	WO AL	DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
					GH GM KE LS MW MZ SD SL SZ TZ UG ZW AM AZ BY KG KZ MD RU TJ TM AT BE CH CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG	
	WO 200127346	P	20010419	WO A1	PUBLICATION OF THE INTERNATIONAL APPLICATION WITH THE INTERNATIONAL SEARCH REPORT	(PUB. OF THE INTERNATIONAL APPL. WITH THE INTERNATIONAL SEARCH REPORT)
\bigcirc	WO 200127346	P	20010613	WO 121	EP: THE EPO HAS BEEN INFORMED BY WIPO THAT EP WAS DESIGNATED IN THIS APPLICATION	
	WO 200127346	P	20010830		REQUEST FOR PRELIMINARY EXAMINATION FILED PRIOR TO EXPIRATION OF 19TH MONTH FROM PRIORITY DATE	
	WO 200127347	P	19991015	WO AA	PRIORITY (PATENT) FI 992234 A 19991015	
	WO 200127347	P	20001013	WO AE	APPLICATION DATA	(APPL. DATA)
					WO 2000FI895 A 20001013	
	WO 200127347	P	20010419	WO AK	DESIGNATED STATES CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED STATES CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
					AE AG AL AM AT AT AU AZ BA BB BG BR BY BZ CA CH CN CR CU CZ CZ DE DE DK DK DM DZ EE EE ES FI FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ PL PT RO RU SD SE SG SI SK SK SL TJ	
کر					TM TR TT TZ UA UG US UZ VN YU ZA	

					ZW	
\bigcirc	WO 200127347	P	20010419	WO	DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
					GH GM KE LS MW MZ SD SL SZ TZ UG ZW AM AZ BY KG KZ MD RU TJ TM AT BE CH CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG	
	WO 200127347	P	20010419	WO A1	PUBLICATION OF THE INTERNATIONAL APPLICATION WITH THE INTERNATIONAL SEARCH REPORT	(PUB. OF THE INTERNATIONAL APPL. WITH THE INTERNATIONAL SEARCH REPORT)
	WO 200127347	P	20010613	WO 121	EP: THE EPO HAS BEEN INFORMED BY WIPO THAT EP WAS DESIGNATED IN THIS APPLICATION	
	WO 200127347	P	20010816		REQUEST FOR PRELIMINARY EXAMINATION FILED PRIOR TO EXPIRATION OF 19TH MONTH FROM PRIORITY DATE	
	WO 200129280	P	19991015	WO AA	PRIORITY (PATENT)	
					FI 992233 A 19991015	
	WO 200129280	P	19991015	WO AA	PRIORITY (PATENT)	
					FI 992234 A 19991015	
	WO 200129280	P	19991015	WO AA	PRIORITY (PATENT)	
					FI 992235 A 19991015	
	WO 200129280	P	19991015	WO AA	PRIORITY CLAIMED	
					US 159799 P 19991015	
	WO 200129280	P	20000118	WO AA	PRIORITY CLAIMED	
					US 176948 P 20000118	
	WO 200129280	P	20000310	WO AA	PRIORITY (PATENT)	
					FI 2000564 A 20000310	
	WO 200129280	P	20001016	WO AE	APPLICATION DATA	(APPL. DATA)
(.)					WO 2000US28537 A 20001016	
	WO	P	20010426	WO	DESIGNATED STATES CITED IN A	(DESIGNATED STATES

	200129280		AK	PUBLISHED APPLICATION WITH SEARCH REPORT	CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
				AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH CN CR CU CZ CZ DE DE DK DK DM DZ EE EE ES FI FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ PL PT RO RU SD SE SG SI SK SK SL TJ TM TR TT TZ UA UG US UZ VN YU ZA ZW	
	WO 200129280	P	20010426 WO AL	DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
				GH GM KE LS MW MZ SD SL SZ TZ UG ZW AM AZ BY KG KZ MD RU TJ TM AT BE CH CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG	
\bigcirc	WO 200129280	P	20010426 WO A1	PUBLICATION OF THE INTERNATIONAL APPLICATION WITH THE INTERNATIONAL SEARCH REPORT	(PUB. OF THE INTERNATIONAL APPL. WITH THE INTERNATIONAL SEARCH REPORT)
	WO 200129280	P	20010620 WO 121	EP: THE EPO HAS BEEN INFORMED BY WIPO THAT EP WAS DESIGNATED IN THIS APPLICATION	
	WO 200129280	P	20010816 WO DFPE	REQUEST FOR PRELIMINARY EXAMINATION FILED PRIOR TO EXPIRATION OF 19TH MONTH FROM PRIORITY DATE	
	WO 200129891	P	19991015 WO AA	PRIORITY CLAIMED	
	WO 200129891	P	20000118 WO AA	US 159799 P 19991015 PRIORITY CLAIMED	
	200127071		2121	US 176944 P 20000118	
	WO 200129891	P	20000824 WO AE	APPLICATION DATA	(APPL. DATA)
				WO 2000US23213 A 20000824	
*)	WO 200129891	P	20010426 WO AK	DESIGNATED STATES CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED STATES CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)

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	WO 200129891	P	20010426 WO AL	DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
				AT BE CH CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE	
	WO 200129891	P	20010426 WO A1	PUBLICATION OF THE INTERNATIONAL APPLICATION WITH THE INTERNATIONAL SEARCH REPORT	(PUB. OF THE INTERNATIONAL APPL. WITH THE INTERNATIONAL SEARCH REPORT)
	WO 200129891	P	20010620 WO 121	EP: THE EPO HAS BEEN INFORMED BY WIPO THAT EP WAS DESIGNATED IN THIS APPLICATION	
	WO	P	19991015 WO	PRIORITY (PATENT)	
	200129893		AA		
				FI 992233 A 19991015	
	WO 200129893	P	19991015 WO · AA	,	
				FI 992234 A 19991015	
\bigcirc	WO 200129893	P	19991015 WO AA	PRIORITY (PATENT)	
				FI 992235 A 19991015	
	WO 200129893	P	19991015 WO AA	PRIORITY CLAIMED	
				US 175799 P 19991015	
	WO 200129893	P	20000118 WO AA	PRIORITY CLAIMED	
				US 176948 P 20000118	
	WO 200129893	P	20000310 WO AA	PRIORITY (PATENT)	
				FI 2000564 A 20000310	
	WO 200129893	P	20001016 WO AE	APPLICATION DATA	(APPL. DATA)
				WO 2000US28654 A 20001016	
	WO 200129893	P	20010426 WO AK	DESIGNATED STATES CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED STATES CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
()				AE AG AL AM AT AT AU AZ BA BB BG BR BY BZ CA CH CN CR CU CZ CZ DE DE DK DK DM DZ EE EE ES FI FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG	

)					KP KR KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ PL PT RO RU SD SE SG SI SK SK SL TJ TM TR TT TZ UA UG US UZ VN YU ZA ZW	
	WO 200129893	P	20010426		DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
					GH GM KE LS MW MZ SD SL SZ TZ UG ZW AM AZ BY KG KZ MD RU TJ TM AT BE CH CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG	
	WO 200129893	P	20010426	WO A1	PUBLICATION OF THE INTERNATIONAL APPLICATION WITH THE INTERNATIONAL SEARCH REPORT	(PUB. OF THE INTERNATIONAL APPL. WITH THE INTERNATIONAL SEARCH REPORT)
	WO 200129893	P	20010620	WO 121	EP: THE EPO HAS BEEN INFORMED BY WIPO THAT EP WAS DESIGNATED IN THIS APPLICATION	
)	WO 200129893	P	20010802		REQUEST FOR PRELIMINARY EXAMINATION FILED PRIOR TO EXPIRATION OF 19TH MONTH FROM PRIORITY DATE	

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